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Infrared Studies of the Oxidation of 2-Propanol on ZnO

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Synopsis. The oxidation of 2-propanol and acetone on ZnO has been studied by IR spectroscopy. Surface isopropoxide was oxidized to acetate and formate ions *via* enolate complex of acetone. Formation of α-diketone-like species was proposed for oxidation with dinitrogen oxide.

By investigation of the reaction of oxygen with olefins, 2-propanol, acetone, and 2-methyloxirane on metal oxides, such as ZnO, MgO, and NiO, by IR spectroscopy,[1–3] it was found that the compounds are oxidized to carboxylates on the surface. No C–C bond scission took place in the oxidation with dinitrogen oxide.[2,3] In order to clarify the mechanism of the oxidation and the role of adsorbed oxygen species, the oxidation of 2-propanol adsorbed on zinc oxide with oxygen or dinitrogen oxide has been investigated by IR spectroscopy.

Details of the apparatus, procedures, and materials were reported.[1–3] After 0.25—0.4 cm^3/g of 2-propanol or acetone had been introduced into the IR cell, the weakly adsorbed reactants were removed by immersing the trap in liquid nitrogen. Oxygen or dinitrogen oxide of 2 kPa was then circulated over the ZnO, the temperature of which being raised in stages. Infrared spectra were recorded at ambient temperature after each treatment of the sample.

The infrared spectrum of 2-propanol adsorbed on the zinc oxide (0.35 cm^3/g) exhibited bands at 2964, 2922, 2866, 1458, 1366, 1165, and 1134 cm^{-1} (Fig. 1a), which did not change significantly on evacuation at 353 K. The bands agree with those due to the surface isopropoxide formed on metal oxides,[1,4–7] confirming the formation of the stable isopropoxide species on zinc oxide.

The temperature of the zinc oxide containing isopropoxide was raised in stages under circulation of oxygen. The bands due to isopropoxide species were slightly reduced in intensity at 353 K and disappeared at 423 K. New bands appearing at 3038, 1576, 1548, 1498, 1428, and 1308 cm^{-1} at 353 K grew with an increase in temperature of the disk to 423 K. Figure 2A shows the change in intensity of these bands with increase in temperature. The behavior is almost the same as that of the reaction of oxygen with propene and 2-methyloxirane on ZnO[2,3] and with 2-propanol on MgO.[1] Thus, the same assignment is applicable. The bands at 2976, 1548, and 1432 cm^{-1} are due to $\nu_{as}(CH_3)$, $\nu_{as}(COO)$, and $\nu_s(COO)$ of surface acetate ions, respectively, and those at 2872, 1576, and 1366 cm^{-1} to the corresponding vibrations of surface formate ions.

The spectra of acetone-d_6 adsorbed on ZnO, pretreated with D_2O, were investigated for the bands at 1498 and 1308 cm^{-1} (Fig. 1de). Bands appearing at 2666, 2502, 2245, 2216, 1464, 1352 cm^{-1} are attributed to the dissociatively adsorbed acetone, *i.e.*, the enolate complex.[7] The bands at 1466 and 1352 cm^{-1} (1498 and 1308 cm^{-1} for acetone) are assigned to the C=O and C=C coupled vibrations of ($O\text{⋯}C\text{⋯}CD_2$)-groups in the enolate complex.[7–10] CD_2= vibrations appeared at 2245 cm^{-1} (3040 cm^{-1} for acetone). The bands at 2666 and 2502 cm^{-1} are due to the surface OD groups. Similar spectra have been reported by Koga, Onishi, and Tamaru,[7] and Nagai and Miyahara.[9] Thus, the bands at 1498 and 1308 cm^{-1} can be assigned to the enolate complex. The change in intensity of the bands with increase in temperature resembles that of the isopropoxide except for the alkoxyl bands. The results together with the fact that acetone was detected during the course of temperature rise of the ZnO containing 2-propanol in the presence of oxygen leads to the following conclusion: 2-propanol is dehydrogenated to form acetone, which was oxidized to acetate and formate ions *via* the enolate complex.

Similar experiments were carried out for isopropoxide adsorbed on ZnO using dinitrogen oxide instead of oxygen. After admission of dinitrogen oxide to the ZnO containing isopropoxide, its temperature was raised in stages. The resulting spectra are shown in Fig. 3. The intensity of the bands due to the isopropoxide

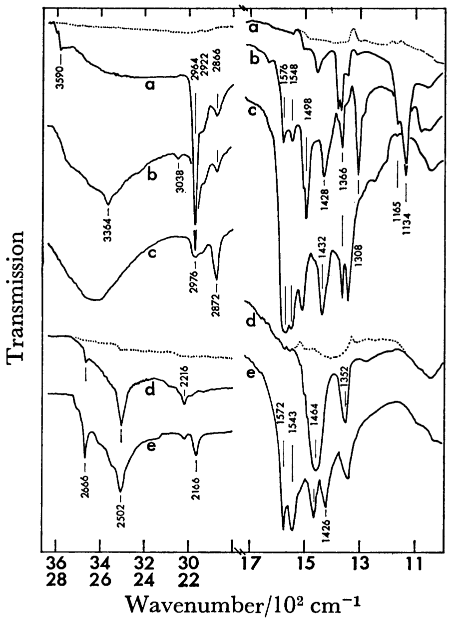

Fig. 1. Interaction of oxygen with 2-propanol or acetone adsorbed on ZnO.
(a) After 1 h adsorption of 2-propanol (0.35 cm^3/g) at 293 K followed by 1 h evacuation at 353 K; (b) followed by 1 h at 393 K in oxygen (2.1 kPa); (c) 1 h at 473 K in oxygen; (d) after 1 h adsorption of acetone-d_6 (0.3 cm^3/g) at 293 K; (e) followed by 1 h at 423 K in oxygen (2.0 kPa). In Figs. 1 and 3, the dotted lines show background spectra.

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decreased with increase in temperature, disappearing completely at 523 K. The bands due to the enolate complex appeared at 353 K and passed through a maximum in intensity at 423 K (Fig. 2B). New bands appeared simultaneously at 1550 and 1436 cm^{-1} at 423 K, the ratio of intensity being constant up to 573 K. This suggests that these bands arise from the same adsorbed species. Results of similar experiments for acetone adsorbed on ZnO are also shown in Fig. 3. Essentially the same spectra are observed except for the alkoxyl bands.

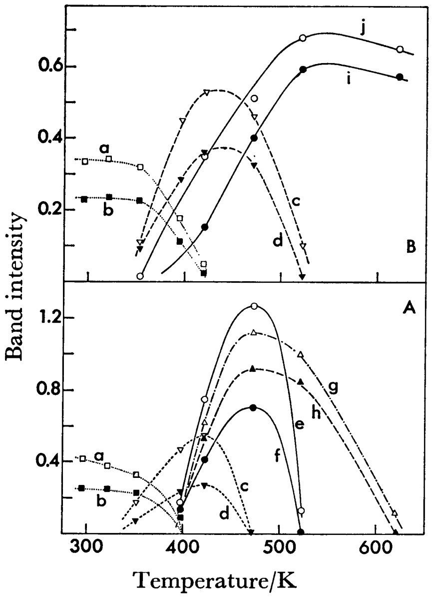


Fig. 2. Change in the band intensities with increasing temperature of ZnO.
(A) In oxygen; (B) in dinitrogen oxide; (a) 2964, (b) 1134, (c) 1498, (d) 1308, (e) 1576, (f) 1366, (g) 1548, (h) 1432, (i) 1550, (j) 1436 cm^{-1}.

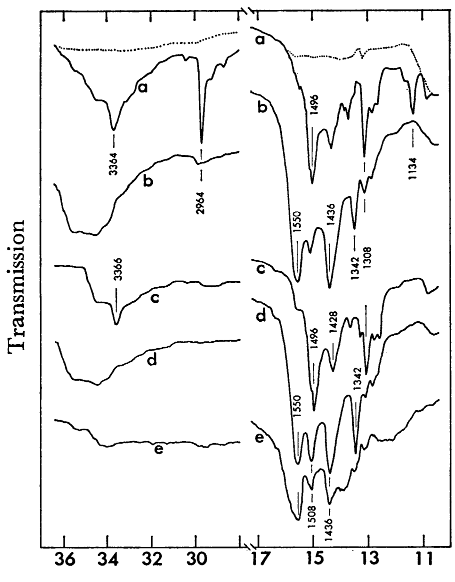
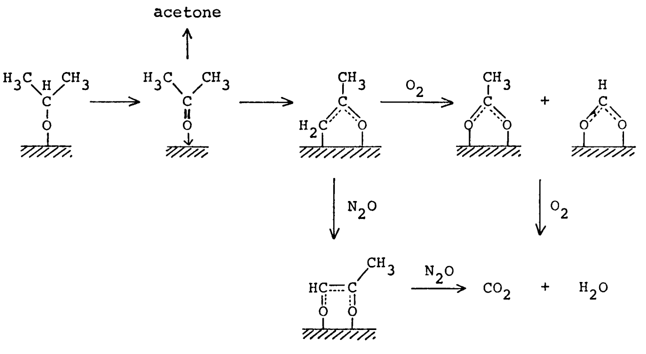


Fig. 3. Interaction of dinitrogen oxide with 2-propanol or acetone adsorbed on ZnO.
(a) After 1 h adsorption of 2-propanol (0.3 cm^3/g) at 293 K followed by 1 h at 393 K in dinitrogen oxide (2.2 kPa); (b) followed by 1 h at 523 K; (c) after 1 h adsorption of acetone (0.28 cm^3/g) at 293 K followed by 1 h at 393 K in dinitrogen oxide (2.3 kPa); (d) followed by 1 h at 523 K in dinitrogen oxide; (e) after 1 h adsorption of biacetyl (0.25 cm^3/g) followed by 1 h at 353 K in oxygen.

It was found in the reactions of dinitrogen oxide with 2-propanol or acetone that an appreciable amount of oxygen had been incorporated by the ZnO before carbon dioxide was formed. In contrast to the oxidation by oxygen, no cleavage of the C–C bond occurred, since no bands due to the formate ions appeared in the COO or CH stretching region. The results together with the change in intensity of the bands with increase in temperature (Fig. 2B) suggests that the enolate complex incorporate oxygen to form a new oxygen-containing compound having absorption at 1550 and 1436 cm^{-1}. Although the position of these bands is very similar to that for propionate ions on ZnO, the intensity of the CH stretching and the bending vibrations of the CH_3 groups is very low, in disagreement with what is expected from the propionate ions. The spectra of a number of oxygen-containing compounds such as alcohols, aldehydes, acids, and ketone were examined. Only biacetyl was found to give essentially the same spectra as those shown in Fig. 3. Thus, these bands are tentatively assigned to α-diketone-like species. Presumably, oxidation proceeds by the following scheme:



Scheme 1.

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